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RADIO CORPORATION OF AMERICA RCA LABORATORIES

THERMOELECTRIC MATERIALS
FOR
POWER CONVERSION

CONTRACT NO. NOBS-84660

PREPARED FOR
BUREAU OF SHIPS
UNITED STATES NAVY
WASHINGTON, D. C.



DAVID SARNOFF RESEARCH CENTER
PRINCETON, NEW JERSEY

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THERMOELECTRIC MATERIALS FOR POWER CONVERSION

Contract No. NOBS-84660

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RADIO CORPORATION OF AMERICA
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PURPOSE


The purpose of this contract is (1) to develop and evaluate materials for the direct conversion of heat to electrical power by thermoelectric means using semiconducting materials and (2) to study the bonding problem so that power generating efficiencies can be demonstrated through the construction of thermocouples.



ABSTRACT

A useful thermoelectric material has been discovered as a result of the research program described in this report. The discovery arose from the measurement of thermal diffusivity at elevated temperatures of a series of heavily doped silicon-germanium alloys. The results showed that at elevated temperatures these materials had a lower conductivity than had been expected on the basis of existing theory. The thermal conductivity values were sufficiently low so that the thermoelectric figure of merit was raised to usefully high values at elevated temperatures. Practical thermoelectric power generators have been made from silicon-germanium alloys. ✓

In addition, this report describes materials research on ternary compounds and alloys, metal trisilicides, and rare earth silicides. Measurements of thermal diffusivity of semiconductors at high temperatures are described together with efficiency measurements on power generating thermocouples.



I. MATERIALS

The efficiency of a thermoelectric power generator depends upon the temperature difference that is maintained across the thermoelectric material. However, the thermoelectric figure of merit ($Z = Q^2/\rho\kappa$) for a semiconducting material usually has a temperature dependence which limits the temperature range over which it is useful for thermoelectric power generation. Since, in general, single materials are not suitable for application over wide temperature ranges, an arrangement of several materials, thermally in series, is required in order to obtain high efficiency. In accordance with the realization that a broad range of materials are required, the research program has involved low, intermediate and high temperature materials.

The methods used to prepare the materials are described individually. The measurements of electrical resistivity, ρ , were obtained from an a-c scanning method while the thermoelectric power Q , and thermal conductivity κ , were measured by subjecting the specimen to a small temperature gradient. Unless otherwise indicated the electronic contribution, κ_{el} , to the total thermal conductivity, κ , was obtained from the Wiedmann-Franz relation

$$\kappa_{el} = S (k/e)^2 T \sigma, \quad (1)$$

where S is a scattering factor having the values of $\pi^2/3$, for degeneracy and impurity scattering, or 2 for non-degeneracy and lattice scattering. In Eq. 1, k is the Boltzmann constant, e is the electronic charge, T is the absolute temperature and σ is the electrical conductivity. The calculated value of κ_{el} was subtracted from κ to obtain lattice contribution, κ_{ph} , since

$$\kappa = \kappa_{el} + \kappa_{ph} \quad (2)$$

for an extrinsic semiconductor.

I-A. TERNARY COMPOUNDS AND ALLOYS

1. AgSbTe_2

In a previous report⁽¹⁾ and in two publications^{(2) (3)} the general properties of semiconducting ternary compounds have been considered. One of the most interesting materials

was AgSbTe_2 , and the study of this compound was continued. The presence of a second phase which was observed in specimens of this material led to the micrographic examination of AgSbTe_2 prepared from the melt by both the Bridgman and Czochralski techniques. In both materials more than one phase was present and the accumulation of evidence suggested that AgSbTe_2 was formed by a peritectic reaction. If one considers the pseudo-binary system, $\text{Ag}_2\text{Te}-\text{Sb}_2\text{Te}_3$, then the phase diagram should have the characteristics shown in Fig. I-1 where the three solid phases α , β , and γ are Sb_2Te_3 , AgSbTe_2 , and Ag_2Te , respectively. The temperatures and composition are approximate, since the work was not sufficiently detailed to establish these parameters definitively. A more detailed study of this system has been reported⁽⁴⁾, and the limiting compositions for the ternary phase, β , were determined to be 41% Ag_2Te - 59% Sb_2Te_3 at both 530° and 400°C. The peritectic temperature at 575°C and the Ag_2Te eutectic at 548°C are in agreement with the values given in Fig. I-1. At lower temperatures it was reported that the ternary phase, β , was unstable with a decomposition point between 350° and 300°C. Although this was not detected during the present work, its existence was not excluded.

The schematic phase diagram reported by Armstrong et al⁽⁵⁾ also indicates that the β -phase is formed by a peritectic reaction, and that there is a eutectic rich in Ag_2Te . However, in contrast to their work the peritectic temperature in Fig. I-1 is probably lower than 595°C and the corresponding liquid phase is richer in Ag_2Te . The eutectoid decomposition temperature for the ternary phase, β , has been reported by Offergeld et al⁽⁶⁾ to be 360°C (not shown in Fig. I-1). They noted that when a specimen of AgSbTe_2 , containing a small amount of Ag_2Te eutectic, was annealed for 15 days at 300°C there was extensive decomposition of the AgSbTe_2 into the eutectoid $\text{Sb}_2\text{Te}_3 + \text{Ag}_2\text{Te}$. As a direct consequence of this it appears that AgSbTe_2 itself has little application as a thermoelectric power generating material.

Compositions rich in Sb_2Te_3 give solids which have a characteristic structure in which a precipitate appears along the $\{111\}$ planes. An example of this is shown in Fig. I-2. It has not been possible to identify the precipitate by x-ray means, in contrast to the Ag_2Te -rich eutectics where the minor phase was positively identified. Also, it has not been possible to prevent the appearance of the precipitate by rapid quenching, nor have any stages of nucleation and growth been observed. These observations suggest that the observed structure arises from a diffusionless solid state transition of the martensite-type rather than a Widmannstätten precipitate as has been suggested⁽⁵⁾. This conclusion has also been reached by Offergeld et al⁽⁶⁾ on the basis of their detailed examination of the phase diagram for this system.

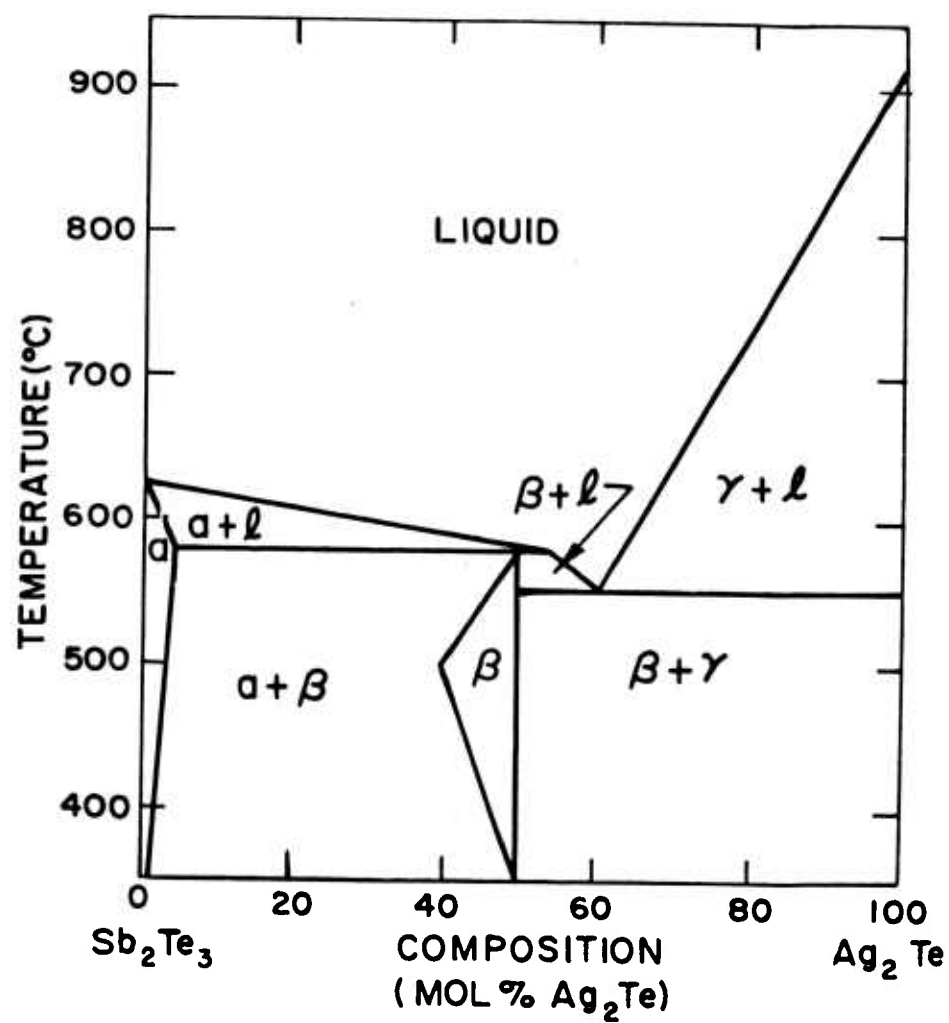


FIG.I-1 TENTATIVE PHASE DIAGRAM FOR THE SYSTEM
 Sb_2Te_3 - Ag_2Te



FIG. I-2 PHOTOMICROGRAPH OF Ag Sb Te_2
CONTAINING EXCESS Sb_2Te_3

2. AgSbTe₂ ALLOYS

The previous examination⁽¹⁾ of the alloy systems of AgSbTe₂ with PbTe, SnTe and GeTe had shown that the most useful materials for use in the vicinity of 500°C were AgSbTe₂-GeTe alloys having a high proportion of GeTe. The methods used to study AgSbTe₂, as described above, were extended to the alloy system. It was found that, in general, the alloys also contain two phases. Those compositions containing more than 50% AgSbTe₂ contain Ag₂Te precipitate similar to AgSbTe₂. Those richer in GeTe have a different precipitate, which has not yet been identified.

Studies have been made of the stability of the alloy, 90% GeTe - 10% AgSbTe₂, when subjected to elevated temperatures in vacuum. A piece of the as-cast alloy was placed in an evacuated sealed ampoule which was heated in a thermal gradient so that the specimen was at 550°C and the other end of the ampoule at 250°C. After 23 hours there was considerable transport of material which was shown by emission spectrographic analysis to be mainly Ge, Sb, and Te. Microscopic examination of the alloy showed that some local melting had occurred. These results suggested that the minor phase present in these alloys was one rich in Sb₂Te₃. Small thermal analysis effects were observed at 350° and 545°C as well as the normal melting at 680°C. The thermal effect at 350°C is probably the rhombohedral to cubic transition of the GeTe-type phase. That at 545°C corresponds closely to the temperature of the eutectic in the system Ag₂Te-Sb₂Te₃. The appearance of the material after heating at 550°C and the thermal effect detected at 545°C show that when the material is used for thermoelectric power generation it should not be heated to above 525°C.

3. PbTe-SnTe ALLOYS

Interest in an n-type material for use in the temperature range above that possible with Bi₂Te₃ alloys led to an examination of the system PbTe-SnTe, which had been shown to exhibit complete solid miscibility⁽⁷⁾. It was known from other work⁽⁸⁾ that PbTe is a useful material in this temperature range; and it was thought that solid solution alloying with SnTe would decrease the lattice thermal conductivity, and thus increase the figure of merit. A study of a number of n-type PbTe-SnTe alloys showed that one of the most promising compositions was 75% PbTe - 25% SnTe which had electrical properties comparable to PbTe.

In order to examine the dependence of lattice thermal conductivity upon composition in the alloy system PbTe-SnTe, specimens of 75% PbTe - 25% SnTe were prepared by the Bridgman method. The thermal and electrical properties of three specimens are shown in Fig. 1-3. The intercept shows that the lattice thermal conductivity, κ_{ph} , for this alloy is

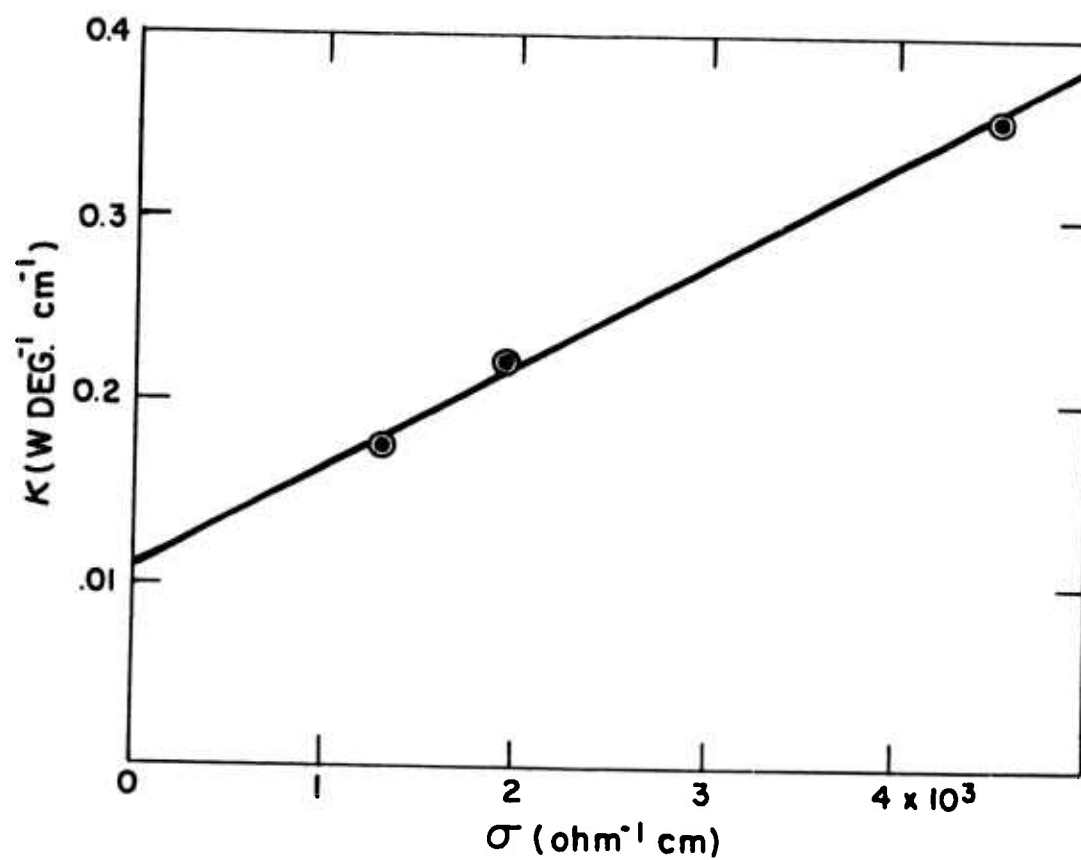


FIG. I-3 THE VARIATION OF TOTAL THERMAL CONDUCTIVITY, κ , WITH ELECTRICAL CONDUCTIVITY, σ , FOR THREE 75% PbTe-25% SnTe ALLOYS

0.011 W deg⁻¹ cm⁻¹. From the slope of the line information about the carrier scattering mechanism can be obtained. From the Wiedemann-Franz relation (Eq. 1), the scattering parameter S is found to be 2.47 which is intermediate between the limiting values of $S = 2$ and $S = \pi^2/3$.

With the value $S = 2.47$ and the temperature dependence of the electrical properties, it was possible to make an estimate of the variation of z with temperature. The thermoelectric power, Q , and the electrical resistivity ρ , were measured at temperatures up to 780°C. The values for κ_{el} were calculated using Eq. 1 assuming that $S = 2.47$, and, as the temperature dependence of S was not known, it was assumed to be invariant. Since S is expected to decrease with temperature, the calculated values for κ_{el} are larger than the true values.

The temperature dependence of the lattice thermal conductivity, κ_{ph} , was assumed to be of the form,

$$\kappa_{ph} = A/(T - \theta/3), \quad (3)$$

where θ is the Debye temperature. The value for the constant A was obtained by assuming that the value for the alloy 75% PbTe - 25% SnTe was the same as for PbTe. The value of A for PbTe was calculated assuming $\kappa_{ph} = 0.018$ W deg⁻¹ cm⁻¹ at 300°K and $\theta = 150$ °K. The total thermal conductivity κ was obtained by adding the electronic and lattice contributions. This assumes no significant ambipolar contribution to the thermal conductivity. The values of Q , ρ , and Z at temperatures up to 780°C are shown in Fig. 1-4 where it is seen that the onset of intrinsic conduction occurs in these specimens at about 700°C, which approximately represents the upper temperature limit for the use of this alloy in power generation. The variation of z with temperature shows a broad maximum which provides an average z value of $\sim 1.3 \times 10^{-3}$ deg⁻¹ over the temperature range 350-750°C. Thermal diffusivity measurements were made upon the alloy and the variation of z with temperature was found to be in very close agreement with that shown in Fig. 1-4.

In order to determine the dependence of lattice thermal conductivity upon composition in the alloy system PbTe-SnTe, a series of specimens of n-type PbTe were prepared. The data were analyzed in the manner described above giving $\kappa_{ph} = 0.016$ W deg⁻¹ cm⁻¹ and $S = 2.64$. The value for κ_{ph} is in fair agreement with a published value⁽⁸⁾ of 0.018 W deg⁻¹ cm⁻¹, and is to be compared with $\kappa_{ph} = 0.011$ W deg⁻¹ cm⁻¹ for the 75% PbTe - SnTe alloy. This shows the extent by which κ_{ph} is reduced by solid solution alloying in this system. The higher value of $S(2.64)$ found for the single component compared with $S = 2.47$ for the alloy is probably a

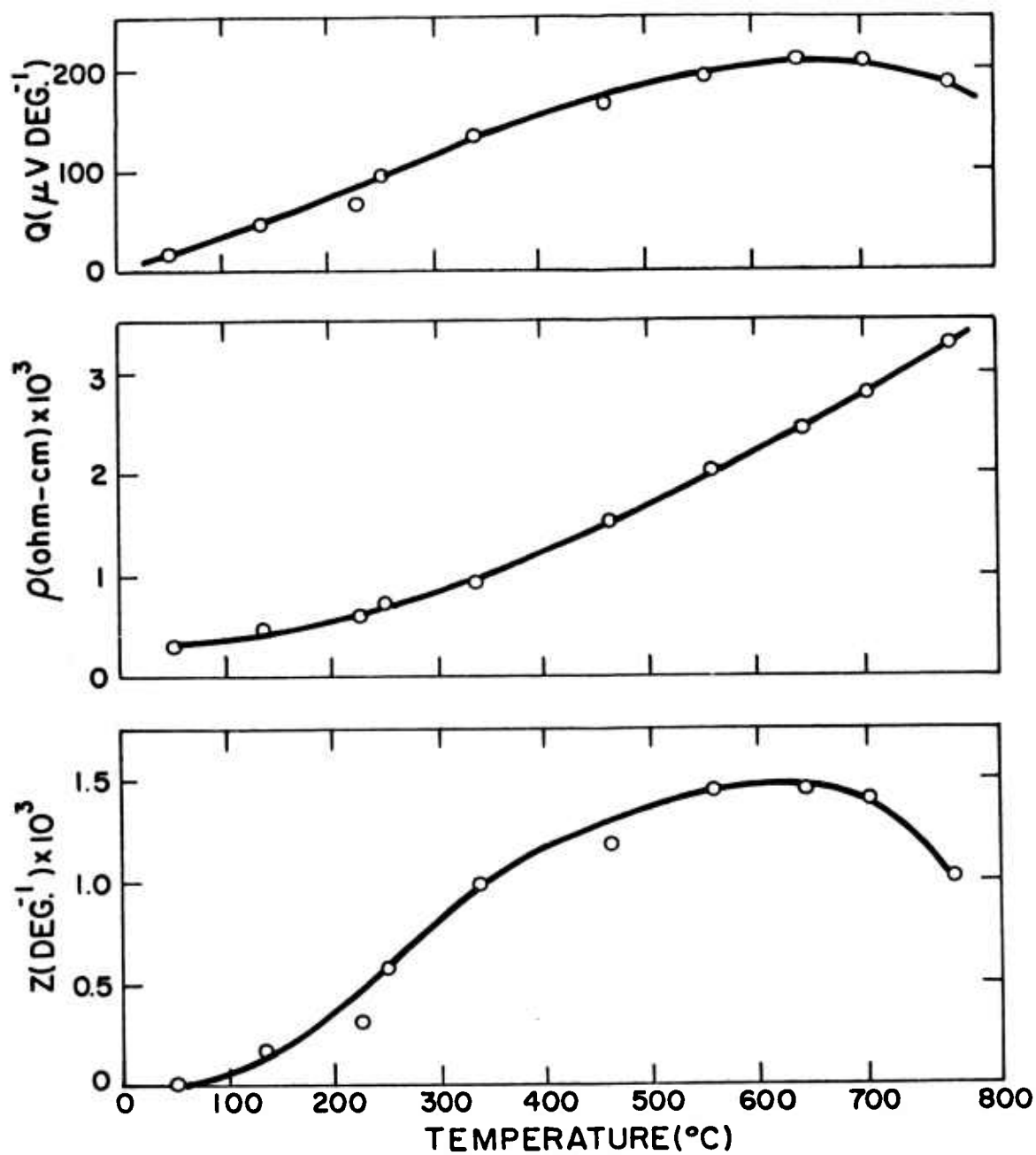


FIG. I-4 THE TEMPERATURE DEPENDENCE OF THERMOELECTRIC PROPERTIES FOR n-TYPE 75% PbTe-25% SnTe ALLOYS

consequence of a small change in scattering mechanism between the two materials rather than an indication of their relative degree of degeneracy. If the latter was the case then the alloy with the larger proportion of SnTe would probably have a higher value of S , and be closer to $S = \pi^2/3$.

The alloy system, PbTe-SnTe, has also been examined with a view to obtaining a p-type material to operate as a generator in the temperature range 200-500°C. This would permit the p-type 90% GeTe - 10% AgSbTe₂ to be replaced with a material which has a good thermal stability under operating conditions, and is better matched thermally to the n-type preferred branch material. The alloy, 75% PbTe - 25% SnTe, was heavily doped with Ag₂Te to provide p-type material,⁽⁹⁾ and the temperature dependence of Q and ρ was obtained. The Q showed a temperature dependence with a useful temperature range too narrow for practical application. This effect is thought to result from the alloy having a small band gap which allows intrinsic conduction to become appreciable within the intended temperature range of operation. This suggests that compositions richer in PbTe would be preferable.

4. SnTe-SnSe ALLOYS

The system, SnTe-SnSe, was investigated for thermoelectric materials for use in the temperature range up to 700°C. It was observed that compositions containing more than 40% SnSe had the mechanical properties and crystal habit of SnSe, a layer-like structure which cleaves readily. X-ray powder diffraction showed that the system has two ranges of limited solid solubility. A cubic solid solution phase extends from SnTe to about 87% SnTe - 13% SnSe, and an orthorhombic phase from 50% SnTe - 50% SnSe to SnSe. The width of the intermediate, eutectic two-phase region decreases with increasing temperature. A supersaturated solution with an orthorhombic structure can be formed at 65% SnTe - 35% SnSe, and annealing at 650°C for 16 hours results in the precipitation of a second phase. For alloys in this region Q and ρ both increased with increasing SnSe, but the values varied upon annealing. The lattice thermal conductivities for some of these materials were about 0.005 W deg⁻¹ cm⁻¹. The Q and ρ were measured at elevated temperatures, and from these a value of z was calculated in the manner previously described. At 650°C the p-type material gave a $z = 0.7 \times 10^{-3}$ deg⁻¹.

A differential thermal analysis investigation of SnTe and the SnTe-SnSe system showed that SnTe is non-stoichiometric with the congruent melting point near the composition SnTe_{1.03}, and that this anion excess exists throughout the SnTe-rich side of the SnTe-SnSe system. However, the thermoelectric properties measured for the composition 60% SnTe - 40% SnSe with excess Te were not significantly improved over those of the

comparable stoichiometric composition. Since these materials have useful values of z only above 600°C, their rate of evaporation into vacuum was measured at this temperature. It was found to be about 3 mg per hour from a specimen of about 5g total weight. Any practical application of these alloys would therefore require that they be encapsulated. Because of this and the fact that the SnTe-SnSe alloys are no superior to PbTe, it is considered that they are unsuitable for use in thermoelectric power generation.

I-B. METAL TRISILICIDES

The study of metal silicides has been extended to include trisilicides in an attempt to obtain refractory materials having less metallic properties than the mono- and di-silicides previously examined⁽¹⁾. Only two metals, iridium and uranium are known to form trisilicides and IrSi₃ was found⁽¹⁾ to have at 1000°C a $\rho^{-1} Q^2$ value higher than MnSi₂ at the same temperature. The latter had hitherto been the silicide with the best high temperature properties. The other trisilicide, USi₃, has now been examined.

The system U-Si has been studied as a source of refractory nuclear fuel elements, but no electrical properties have been reported. The published phase diagram⁽¹⁰⁾ shows USi₃ as a peritectic compound decomposing at 1510°C to USi₂ and a melt, with the liquidus for the USi₃ composition occurring at about 1600°C. The compound has a simple cubic structure (Cu₃Au type) with a lattice parameter of 4.03 Å.

The uranium used in the preparation of USi₃ was in the form of turnings and was cleaned by etching in 1:1 HNO₃. Spectrographic analysis gave a total impurity content of about 0.1%. Chips of Si (99.99%) were used as received. Stoichiometric amounts of the elements were placed in a beryllia crucible in alternate layers with a Si layer on the bottom. Melting was accomplished by direct induction RF heating under argon at about 1/2 atm. The ingot was frozen by slowly reducing the RF power. The cooled ingot was inverted and remelted several times to achieve mixing. It was found that prolonged heating of the melt was inefficient at mixing because of the viscous nature of the melt, and should be avoided because of the increased possibility of crucible contamination. Spectrographic analysis showed 0.01% to 0.1% beryllium in the product. Alumina and boron nitride were also used as crucible materials but they reacted with the melt much more than beryllia.

The ingots were then recast by zone melting in a beryllia boat, and this provided material with good mechanical properties and of more favorable geometry for cutting samples. Attempts to prepare USi₃ in a boat from the elements were unsuccessful because of poor RF coupling.

X-ray analysis showed that a zone melted ingot had three distinct portions. The head or first portion to freeze consisted of USi_3 and a large amount of $\alpha\text{-USi}_2$, the large central portion was of single phase USi_3 and the tail consisted of USi_3 and Si. This is to be expected with zone solidification of a peritectic compound,⁽¹¹⁾ and thus is consistent with the reported phase diagram⁽¹⁰⁾. A metallographic examination was also carried out, and Fig. I-5 shows photomicrographs of the head and center portions of a zone cast ingot of USi_3 . The polished specimens were etched in 1% HF for 3 minutes.⁽¹²⁾ In Fig. I-5a it is seen that the etchant reveals the large amount of αUSi_2 as identified by x-ray analysis. In the central part of the ingot the αUSi_2 is reduced to about 1%.

The electrical resistivity of a specimen of USi_3 was 6×10^{-5} ohm-cm with a thermoelectric power of $-7 \mu\text{V deg}^{-1}$ at room temperature. Unlike IrSi_3 the value was not affected by annealing at temperatures up to 1150°C for 20 hours. The temperature dependence of these properties as measured on one specimen up to 700°C are shown in Fig. I-6. The optimum properties that might be expected from this specimen at 1000°C have been estimated by the linear extrapolation indicated. Table I-1 shows a comparison of these extrapolated values with the measured values⁽¹⁾ for IrSi_3 and MnSi_2 . Values for κ_e were calculated from Eq. 1 assuming degeneracy ($S = \pi^2/3$). In spite of the high θ and κ_e values, it can be seen from Table I-1 that the $Q^2\sigma$ product is significantly larger than for the other silicides.

TABLE I-1
THERMOELECTRIC PROPERTIES OF SILICIDES AT 1000°C

MATERIAL	Q ($\mu\text{V deg}^{-1}$)	σ ($\text{ohm}^{-1}\text{cm}^{-1}$)	$Q^2\sigma$ ($\text{W deg}^{-2}\text{cm}^{-1}$)	(κ_e) ($\text{W deg}^{-1}\text{cm}^{-1}$)
USi_3	+29*	4000*	3.4×10^{-5}	.13
IrSi_3	+45	1470	3.0×10^{-6}	.046
MnSi_2	-40	430	6.9×10^{-7}	.014

*extrapolated value

I-C. RARE EARTH SULFIDES

In continuation of the work previously reported⁽¹⁾ additional rare earth sulfides having the thorium phosphide crystal structure were synthesized. In addition to Ce_2S_3 and Nd_2S_3 , the compounds, La_2S_3 , Pr_2S_3 and Sm_2S_3 , were prepared by the reaction of H_2S with



(a)



(b)

0.1mm

FIG. I - 5 PHOTOMICROGRAPHS OF PORTIONS OF A ZONE CAST
INGOT OF USi_3 . (a), HEAD (b), CENTER

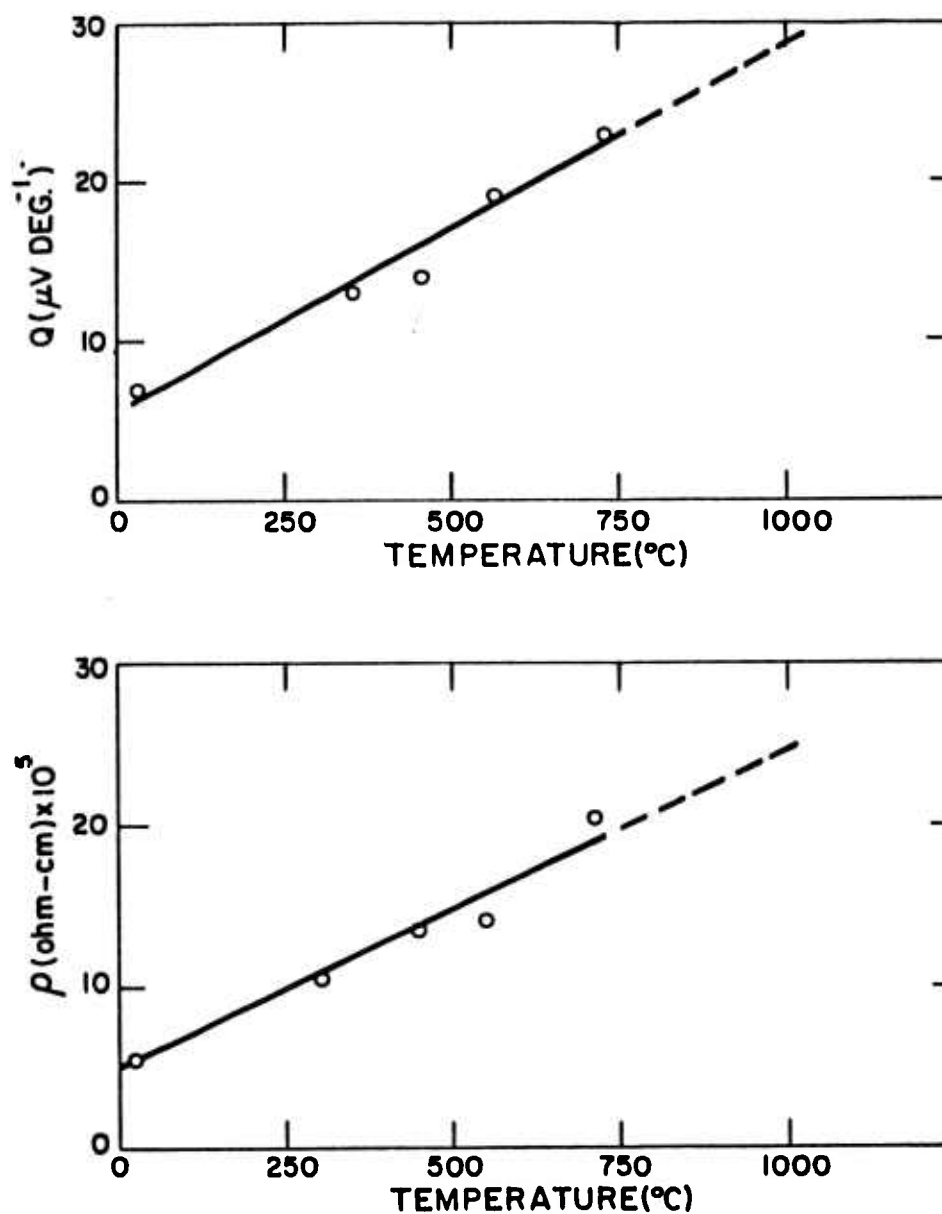
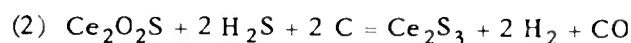
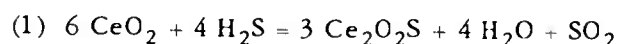
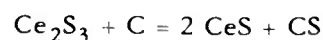


FIG. I- 6 TEMPERATURE DEPENDENCE OF THE THERMOELECTRIC POWER, Q , AND ELECTRICAL RESISTIVITY, ρ , FOR USi_3

the respective oxides using the experimental method previously described. The preparation of Ce_2S_3 was studied in detail in order to establish reproducible conditions for synthesis. Reaction time, temperature, H_2S flow rate and crucible material appeared to be the most critical variables. When the reaction was carried out at temperatures below 1300°C , appreciable amounts of cerium oxysulfide, $\text{Ce}_2\text{O}_2\text{S}$, were formed along with Ce_2S_3 . For complete conversion of the oxide to the sulfide it was necessary to maintain the reaction temperature at 1400°C for about three hours. Under these conditions a H_2S flow rate of 1.5 cubic feet/hour was sufficient for the complete reaction of one hundred grams of ceric oxide. When a silica crucible was used in place of carbon, $\text{Ce}_2\text{O}_2\text{S}$ was the major product. These results support the hypothesis⁽¹³⁾ that the reaction proceeds in two steps:



The formation of traces of CeS probably proceeds by the reduction of Ce_2S_3 with carbon:



Electrically conducting, fused ingots of cerium sulfide and samarium sulfide were prepared by RF heating. From crack-free portions of these ingots, specimens suitable for the measurement of electrical properties and of thermal conductivity were obtained. Data from the x-ray investigation, metallographic examination, spectrographic analysis, chemical analysis and thermal conductivity measurements on these specimens are listed in Table I-2.

TABLE I-2
PROPERTIES OF RARE-EARTH SULFIDES AT 300°K

COMPOUND	SAMPLE	MINOR PHASES	TOTAL METALLIC IMPURITIES (ppm)	CHEMICAL ANALYSIS	κ ($\text{W deg}^{-1} \text{cm}^{-1}$)	κ_{ph} ($\text{W deg}^{-1} \text{cm}^{-1}$)
Ce_2S_3 - Ce_2S_4	F-9	6% CeS 1.5% carbon	35	$\text{S/Ce} = 1.27$	0.0244	0.0108
Ce_2S_3 - Ce_3S_4 (fused)	F-13	1% carbon	410	$\text{S/Ce} = 1.42$	0.0178	0.0116
Sm_2S_3 - Sm_3S_4 (fused)	F-10	1% SmS 1% carbon	600	$\text{S/Sm} = 1.41$	—	—

The major phase in each of these specimens was the rare-earth metal sulfide having the thorium phosphide structure. Small amounts of carbon and rare earth monosulfide were also present as minor phases.

The temperature dependence of the electrical properties are shown in Figs. I-7, I-8, and I-9. Calculated values of the figure of merit are plotted as a function of temperature in Fig. I-10. In calculating the figure of merit over the temperature range in Fig. I-10, the total thermal conductivity, κ , was obtained by calculating κ_{e_i} from the measured values of resistivity using Eq. (1) and assuming that κ_{ph} is independent of temperature. The value of κ_{ph} was obtained by subtracting κ_{e_i} from the total measured thermal conductivity κ at room temperature. In calculating κ_{e_i} at each temperature, the samples were assumed to be degenerate. It seems reasonable that these assumptions lead to a conservative estimate of the figure of merit, particularly at the highest temperatures.

There is a striking difference in the temperature dependence of the electrical properties of cerium sulfide and samarium sulfide, in spite of the fact that both compounds have the thorium phosphide crystal structure. Recent measurements⁽¹⁴⁾ of magnetic susceptibility and lattice constant of cerium sulfide and samarium sulfide suggest that the difference in electrical properties is probably due to the fact that samarium is present in two valence states, in contrast to cerium which is present in only one. The formulae for the thorium phosphide structure phase-region of the two compounds may be represented as $\text{Sm}_2^{\text{III}}\text{Sm}^{\text{II}}\text{S}_4$ and $\text{Ce}_2^{\text{III}}\text{S}_3\text{-Ce}_3^{\text{III}}\text{S}_4$. In filling the metal defects of the thorium phosphide structure, each cerium atom enters the lattice as a trivalent ion and donates one free electron for electrical conduction. Samarium, however, enters the lattice primarily in the divalent state, and contributes no free electrons for conduction. The resistivity of cerium sulfide (Figs I-7 and I-8) shows a linear increase with temperature, similar to that of a metal. The resistivity of samarium sulfide (Fig. I-9) decreases with increasing temperature, probably due to thermal excitation of electrons from divalent samarium ions.

It has been reported⁽¹⁵⁾ that the scandium sulfides Sc_2S_3 and ScS both crystallize in the simple NaCl type structure, with nearly the same lattice parameter. Therefore, it seemed probable that a complete series of solid solutions $\text{Sc}_{2+x}\text{S}_3$ ($0 < x < 1$) exist, in which the vacant scandium sites in Sc_2S_3 are progressively filled. The thermoelectric properties of this system of solid solution alloys are of interest for two reasons. First, it has been found that compounds crystallizing in the NaCl structure usually have a low lattice thermal conductivity⁽¹⁾. Second, it should be possible to vary the electrical properties from insulating to metallic, if the scandium is trivalent in both Sc_2S_3 and ScS .

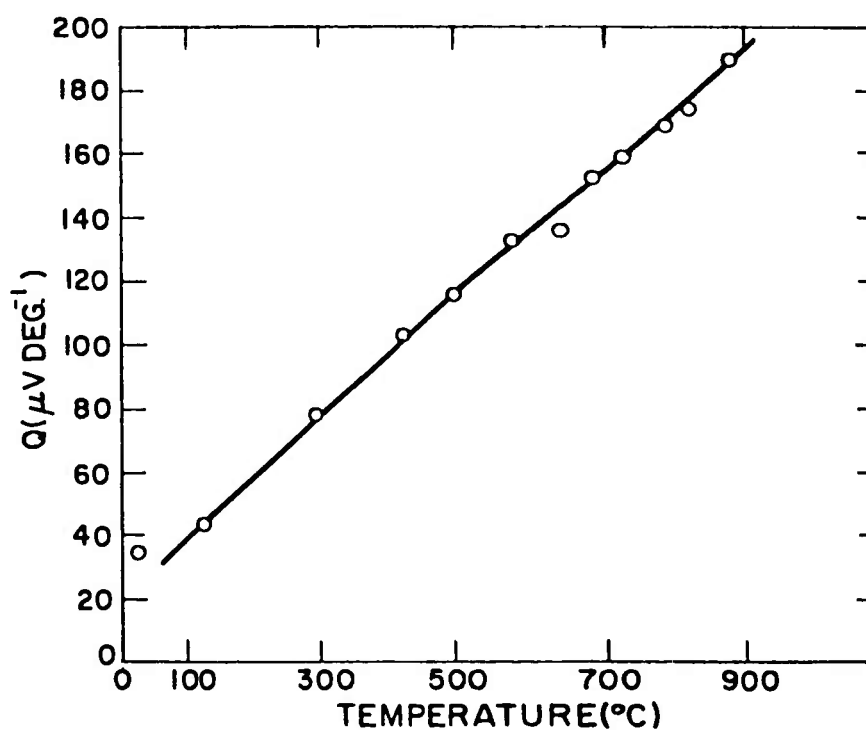
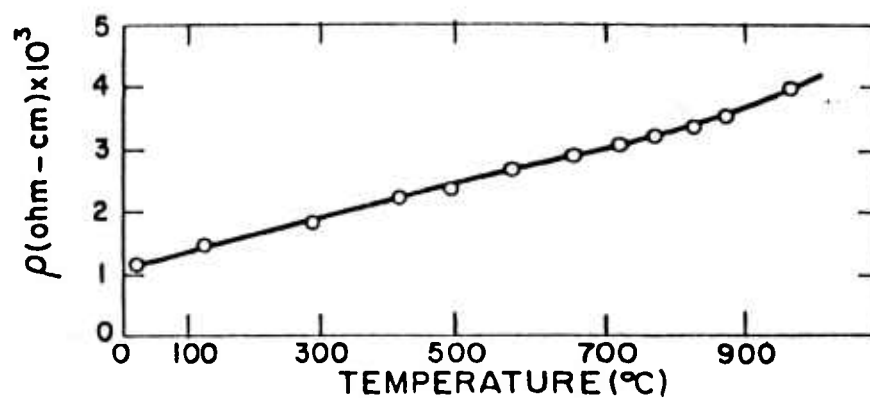


FIG. I- 7 TEMPERATURE DEPENDENCE OF RESISTIVITY, ρ , AND THERMOELECTRIC POWER, Q , OF CERIUM SULFIDE SAMPLE F-13

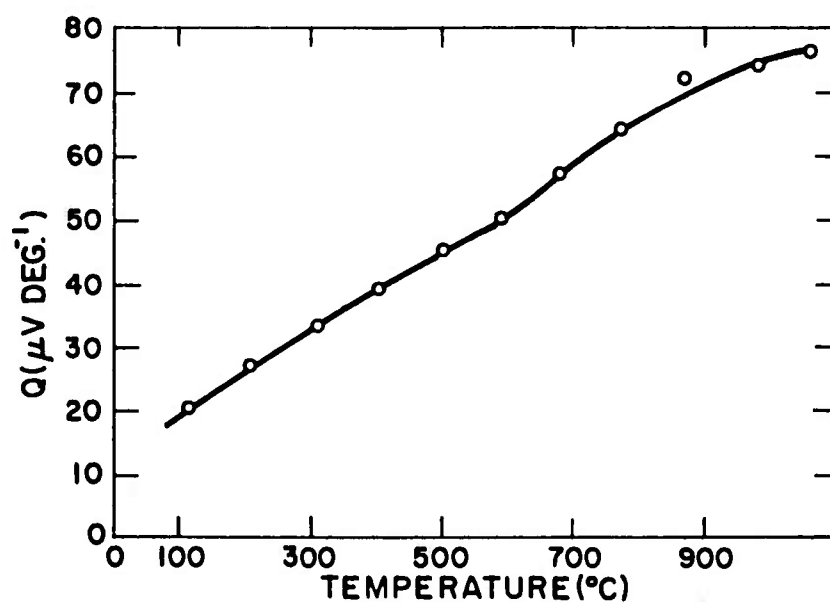
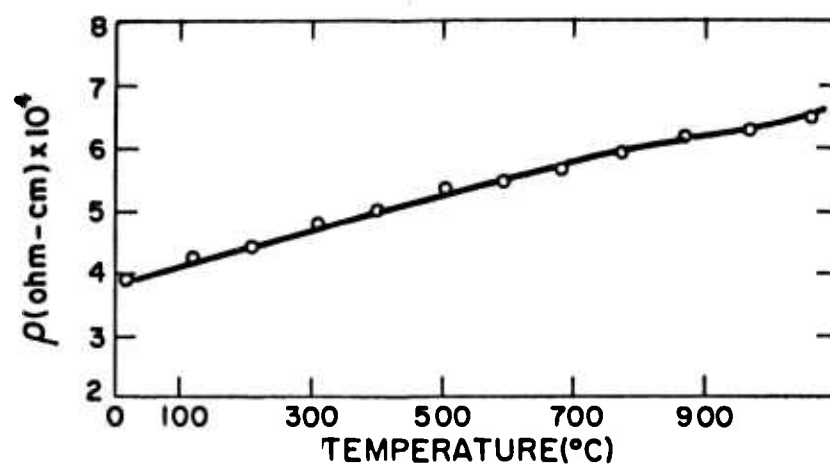


FIG. I-8 TEMPERATURE DEPENDENCE OF RESISTIVITY, ρ , AND THERMOELECTRIC POWER, Q , OF CERIUM SULFIDE SAMPLE F-9

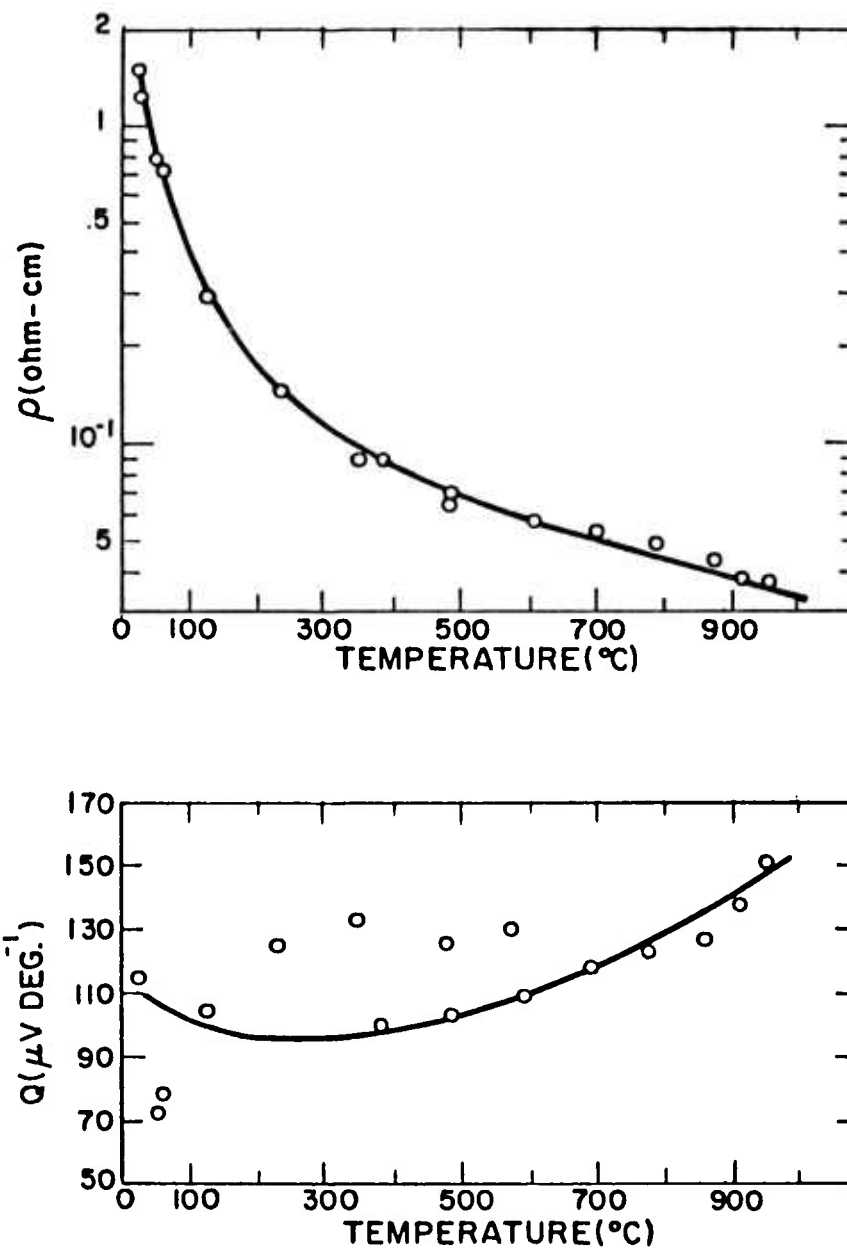


FIG. I-9 THE TEMPERATURE DEPENDENCE OF RESISTIVITY, ρ , AND THERMOELECTRIC POWER, Q , OF SAMARIUM SULFIDE SAMPLE F-10

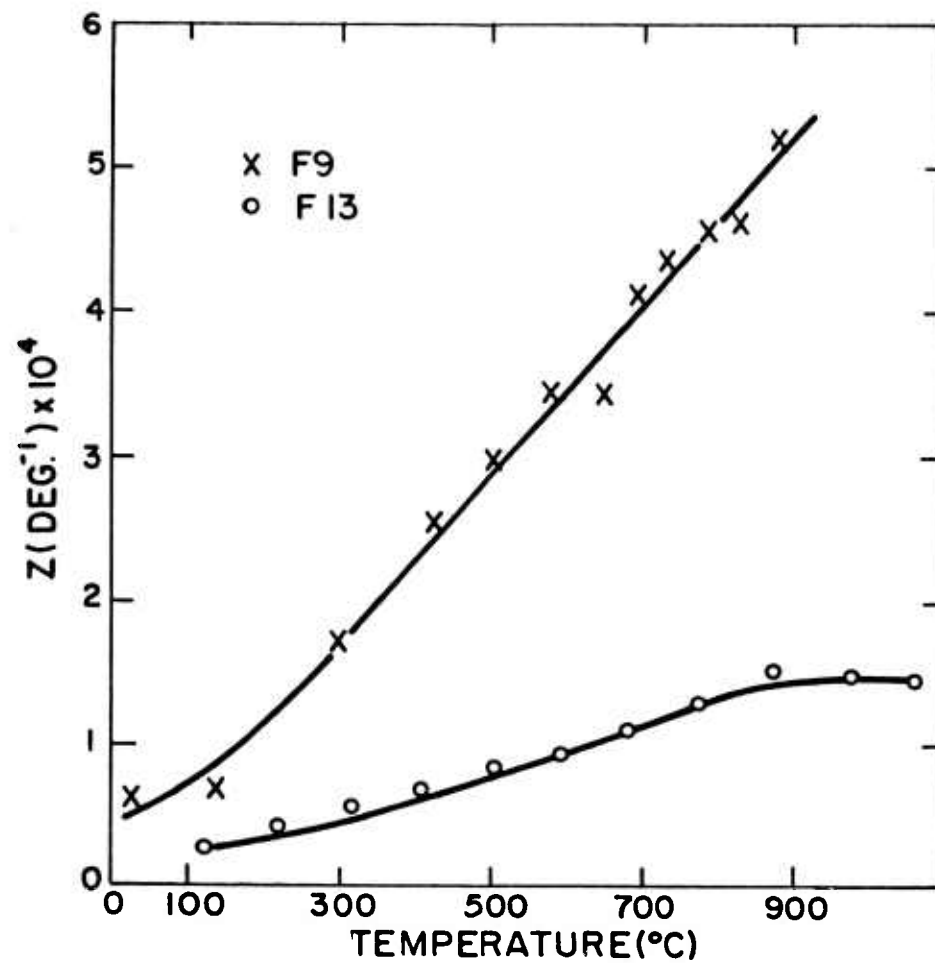


FIG. I-10 THE TEMPERATURE DEPENDENCE OF THE FIGURE OF MERIT, Z, OF TWO SAMPLES OF CERIUM SULFIDE

Only meager information concerning the preparation and properties of scandium sulfide was found in the literature. Therefore, the method successfully employed for the preparation of rare-earth metal sulfides was used. The reaction of Sc_2O_3 with H_2S gas in a carbon crucible was first carried out at 1400°C . Examination of an x-ray powder pattern showed that the major product had the NaCl structure ($a = 5.20 \text{ \AA}$), but that appreciable amounts of an unidentified phase, or phases were also present. Subsequent re-reaction at 1600°C yielded an improved material, which probably contained about 5% of a second phase (possibly $\text{Sc}_2\text{O}_2\text{S}$). Microscopic examination showed that the major phase is dark brown and opaque, and that the minor phase is light yellow and transparent. The scandium sulfide was ground to a powder, mixed with 5% naphthalene as a binder, and pressed into a rectangular bar. After removal of the naphthalene at 100°C in vacuum, the bar was sintered by RF heating at 1600°C in vacuum for four hours. The sintering technique was adapted from that described for cerium sulfide. The electrical properties of the sintered materials at room temperature were $Q = -12 \mu\text{V}/^\circ\text{C}$ and $\rho = 2.99 \times 10^{-4} \text{ ohm-cm}$. Measurements as a function of temperature showed that some irreversible effects took place during the first heating cycle as the room temperature ρ changed to $6.16 \times 10^{-4} \text{ ohm-cm}$ after heating. During the second heating cycle no further hysteresis effects were observed. The values of Q and ρ were obtained up to 964°C , and these indicated that scandium sulfide shows little promise as a material for thermoelectric power generation.

I-D. SILICON-GERMANIUM ALLOYS

The discovery that Si-Ge alloys possess properties for thermoelectric power generation superior in several ways to previous materials, led to an investigation of some methods for their preparation. The material was required in the form of dense, mechanically strong, polycrystalline ingots having homogeneous compositions within the Si-Ge solid solution alloy system. It was also necessary that the method could be used to provide a uniform distribution of a doping agent at a relatively high concentration. These considerations led to the conclusion that the preparative method should be one involving growth from a melt.

The Si-Ge binary system was first investigated by Stohr and Klemm⁽¹⁶⁾, and their phase diagram is shown in Fig. I-11. The system forms a complete series of solid solutions with no intermediate compounds and has a considerable separation between the liquidus and solidus curves. Thus, when an alloy melt of uniform composition is cooled, the solid shows a variable composition, ranging from the corresponding solidus value down to pure Ge. This is not the equilibrium situation but the time required to reach equilibrium at each successive stage of cooling is prohibitively long, as solid state diffusion in these materials is very slow.

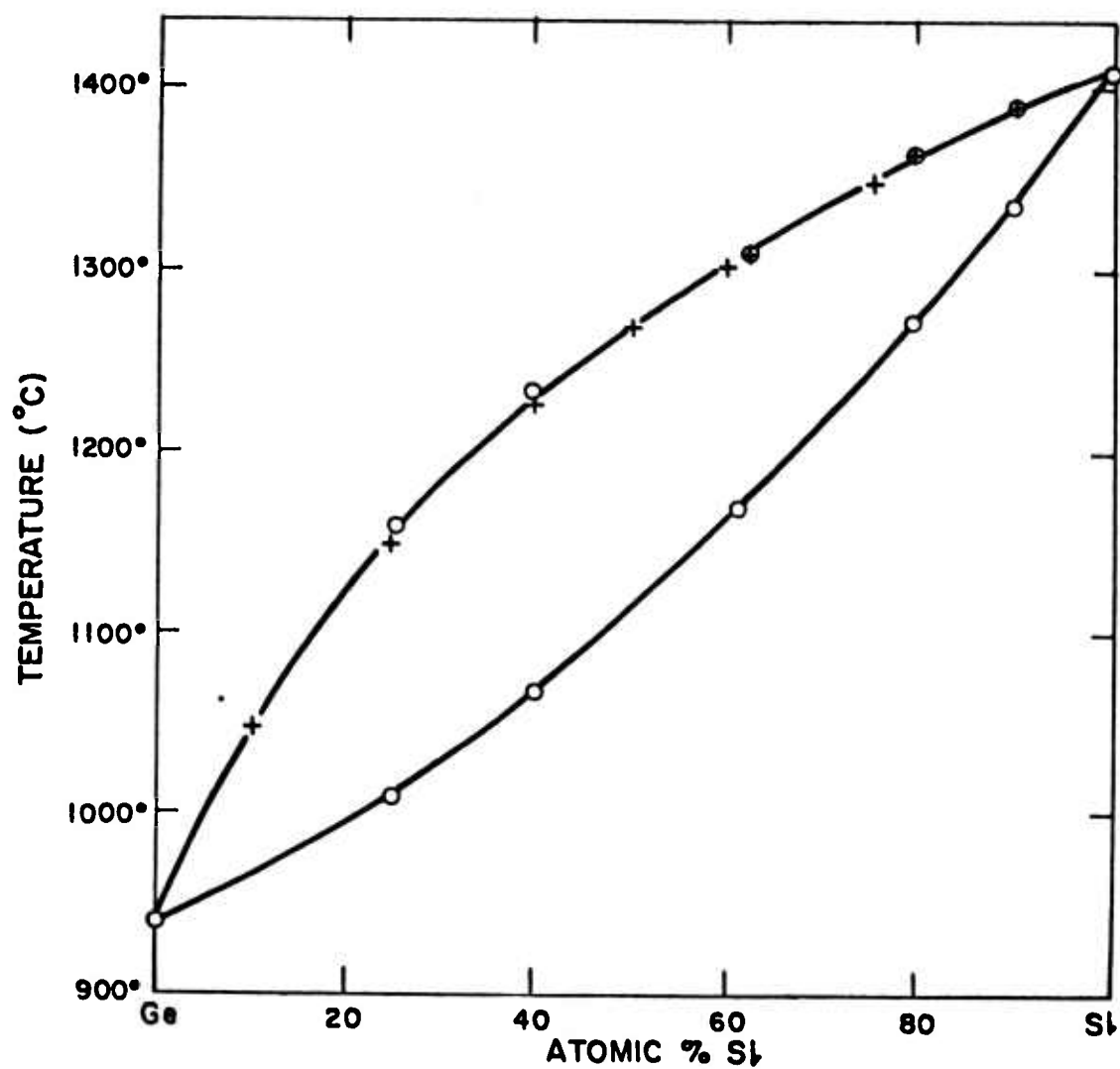


FIG. I-II THE PHASE DIAGRAM FOR THE Ge-Si SYSTEM

Hence, in order to prepare a solid of uniform composition a melt of the corresponding liquidus composition must be frozen isothermally, and the composition of the melt must not change during the process. This can be achieved by adding material (having the average composition of the product) to the melt at the same rate as the product is being withdrawn. Techniques which maintain constant composition in the melt include the feed inpull-out modification of the Czochralski crystal pulling method and zone melting, using either a boat or a floating zone.

The horizontal zone melting method has the merit of simplicity, and it was developed to prepare Si-Ge alloys. At one end of a boat there was placed material which had a composition corresponding to the desired liquidus and the remaining portion of the boat contained material having the composition of the solidus. The boat was sealed in a quartz ampule and supported in a fixed position so that a zone furnace could be moved slowly along the ampoule. Under these conditions, the material freezing behind the liquid zone had the same composition as that melting into it, so that the composition of the zone remained constant until near the end of the boat, or the last portion to freeze.

The homogeneity of the alloy composition depends upon growth rate, the thermal gradient at the growth interface, the rate of diffusion in the melt, stirring of the melt, the thermal stability of the furnace and the uniformity of the starting materials.

The growth rate must be slow enough, so that the Si that is constantly being depleted in the liquid at the advancing growth interface can be supplied from the material that is being melted into the liquid zone at the receding interface. The rate of supply is probably determined by diffusion at the growth interface and not by the rate of convective circulation in the majority of the melt.

Temperature fluctuations in the zone furnace cause the position of the solid-liquid interface to move, thus changing the effective growth rate. The displacements caused by this effect can be reduced by increasing the thermal gradient in a direction perpendicular to the growing interface.

The polycrystalline Si-Ge alloy ingots prepared by the zone melting technique consisted of large grains approximately $1\text{ mm} \times 1\text{ mm} \times 5\text{ mm}$, usually oriented with the long axis at a small angle to the direction of growth. The upper surface of the ingot was marked with a striation pattern which indicated the topography of the solid-liquid interface. The lower surface of the ingot closely followed the shape of the boat in which it was grown.

Room temperature thermoelectric power and resistivity values for some doped specimens of Si-Ge alloy having approximately similar compositions are shown in Table I-3.

TABLE I-3
THERMOELECTRIC POWER, Q ,
AND RESISTIVITY, ρ , OF SOME Si-Ge ALLOYS

SAMPLE	Q vs. Cu (μ V deg $^{-1}$)	ρ (ohm-cm)
S 1185 K	305	5.4
S 1196 D	150	1.30
JPD 14-O	157	1.22
JPD 14-X	170	1.50
S 1186-X	220	2.76
JPD 14-C	162	1.40

The variation of the electrical properties is probably due more to variation of impurity concentration, than to minor variations in alloy composition. The temperature dependence of the thermoelectric properties showed that this material was useful for thermoelectric power generation.

The compositions of the ingots were examined to determine (1) alloy composition or Si-Ge ratio, (2) doping concentration and (3) the presence and concentration of any residual impurities. The alloy composition could be determined by quantitative chemical analysis, but this is difficult due to the chemical similarity of Ge and Si. For this reason the composition was obtained from both lattice parameter and density measurements, and from x-ray fluorescence analysis. The lattice parameters were measured from x-ray powder diffraction photographs, and the densities were determined by weighing samples having simple geometries. The two curves* (composition vs lattice parameter and composition vs density) were drawn using available data,^(16, 17, 18) and were then corrected to make them consistent with one another, allowing a range of $\pm 1\%$ Si for each method. The x-ray fluorescence method was calibrated using Si-Ge samples whose compositions had been determined from lattice parameter measurements.

The three methods of analysis, (lattice parameter, density and x-ray fluorescence) gave values for the composition averaged over the quantity of the sample that is measured. Hence, a complete series of measurements gives information about compositional variations related to the sizes of the samples. The samples for x-ray powder diffraction were obtained from a slice 0.030 inch thick cut completely across the ingot perpendicular to the growth

direction. The whole slice was ground and mixed and the powder specimen was taken from this material. The densities were measured on specimens having a volume of about 1 cm³; and the x-ray fluorescence data refers to a sample, 0.25 inch square and 0.01 inch thick.

A comparison between the three methods of analysis is shown in Table I-4. The agreement is good considering the different sample sizes involved. These three methods were used to estimate the variation in composition that occurred along the length of an

TABLE I-4
COMPOSITIONAL VARIATIONS IN Ge-Si ALLOY INGOTS
HAVING APPROXIMATELY THE SAME COMPOSITION

SPECIMEN	SAMPLE	COMPOSITIONAL DEVIATION FROM AVERAGE (at % Si)		
		DENSITY	LATTICE PARAMETER	X-RAY
A	1	+1.3	-0.8	+0.2
	2	+1.8	+0.0	+0.4
	3	+0.9	+0.4	-0.3
	4	+1.4	-0.8	+0.1
B	1	+1.1	+0.2	-0.2
C	1	+2.3	+2.0	+0.3
	2	-0.8	-0.7	-1.6
	3	-2.5	-2.5	-3.7
D	1	-2.4	-2.4	-3.6
	2	+0.7	-0.3	-0.7

ingot. It was found that the composition varied on the average by about 0.5% Si per inch, although specimens were often obtained in which the uniformity was superior to this. The preparation of uniform specimens indicates that the phase diagram of Stohr and Klemm (Fig. I-11) is essentially correct, and that the compositional variations observed along many ingots are not an inherent consequence of the method.

The estimation of the concentration of the doping agent in the alloys can not be obtained from carrier concentration measurements by the Hall effect, since in the range of interest they are not equivalent. The methods used for analysis included emission spectrographic, wet chemical and x-ray fluorescence techniques. These methods showed that the p-type material was uniformly doped along the length of the ingots. The n-type material, in general, had an impurity concentration which varied within a factor of two along an ingot. The variation was probably a result of changes that occurred in the vapor pressure of the impurity within the ampoule during growth.

The presence of residual impurities were detected but these were at a much lower concentration than the doping agents. The only regularly occurring impurities detected were Al, Cu, Fe and Mg; and of these, only Al occurred in concentrations greater than 10 ppm. The only additional elements detected by mass spectrographic analysis were Be and Ca, both at less than 1 ppm. The low impurity content is a direct consequence of the use of zone melting.

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II. THERMOELECTRIC POWER GENERATION

II-A. TELLURIDE MATERIALS

Thermoelectric power generating thermocouples constructed in the segmented arrangement described in a previous report⁽¹⁾ and illustrated in Fig. II-1 have been subjected to life tests of limited duration. These preliminary tests have given encouraging results. The relatively small amounts of materials which were then available, and also the fact that many other effects were under study led to the duration of the tests being limited to about 300 hours. During such periods the majority of the tests indicated very little change in the original electrical properties.

The tests, however, revealed the following limitations in the material properties which appear when they are used for device fabrication:

1. The p-type 90% GeTe — 10% AgSbTe₂ alloy has a tendency to evaporate at temperatures above 500°C. The ambient in which evaporation was observed was forming gas (93% N₂ — 7% H₂) at atmospheric pressure. Emission spectrographic analysis of the deposit showed that it contained germanium and silver.
2. The n-type 75% PbTe — 25% SnTe alloy, while superior to PbTe as to thermoelectric properties, exhibited fractures which may arise from a relatively high coefficient of thermal expansion.
3. In the preparation of the 48 thermocouples required for a 25 W generator, it has been necessary to test the resistivity and thermoelectric power of each segmented thermoelement. This led to the replacement of at least 50% of the required thermoelectric material. Subsequent preparations gave material of improved mechanical quality and with a higher yield of useful material.

In efforts to reduce the evaporation noted above, preliminary experiments have indicated that encapsulation by various ceramic coatings applied in aqueous suspension and then fired do not exhibit sufficient adhesion to withstand the forces exerted by the vapor pressures. In order to examine the conditions under which the evaporation takes place a pressure chamber was constructed and the effects of ambient gas composition, pressure, and temperature were studied. Forming gas (7% H₂ — 93% N₂) was used at pressures up to

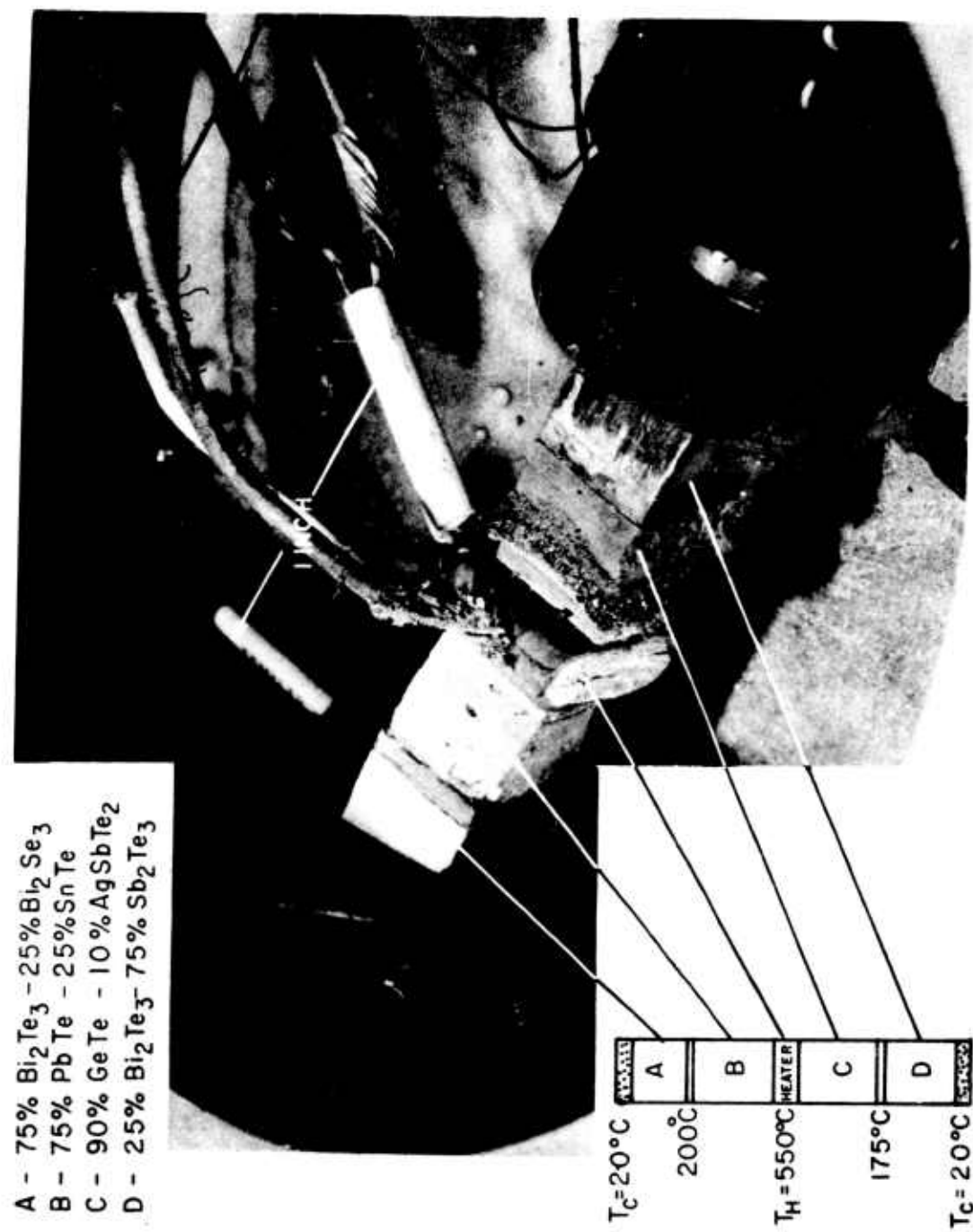


FIG. II - I PHOTOGRAPH OF SEGMENTED POWER GENERATING THERMOCOUPLE

7 atmospheres and the contact surfaces were varied, but neither prevented the evaporation nor the build-up of reacted layers over the contacting area.

A 48-couple generator was assembled using two materials in each branch of the thermocouples. The n-type branches consisted of 75% Bi_2Te_3 - 25% Bi_2Se_3 and 75% PbTe - 25% SnTe alloys, and the p-type branches consisted of 75% Sb_2Te_3 - 25% Bi_2Te_3 and 90% GeTe - 10% AgSbTe_2 alloys. The metal-semiconductor bonds at the cold and intermediate junctions for both the p- and n-type materials were made by soldering, while pressure contacts were used for the hot-junctions. Heat was applied to the hot junction by a wire-wound resistance heater, and the cold junctions maintained at 20°C by circulating water. The maximum efficiency obtained was 11.4% with 21 W output at a hot junction temperature of 625°C. Measurements on a single couple had previously⁽¹⁾ given an efficiency of ~ 12%, when operating with a hot junction temperature of 550°C. Subsequent results on the 48 couple generator showed that a radical change in performance occurred at about 560°C, which apparently is the temperature limit of stability for the 90% GeTe - 10% AgSbTe_2 alloy. The difference in performance between the single couple and the generator arose from excessive electrical resistance at the hot junctions in the latter.

Although the wedge shaped form of the thermoelectric material helps in designing for low stray heat losses, certain spacing allowances were made. It has been found that greater care in minimizing spacings must be observed at the temperatures involved, since the radiative heat transfer is very substantial.

Other experiments showed that Bi_2Te_3 could be used as a bonding material between PbTe - SnTe alloy and stainless steel, and gave junction resistance comparable to that obtained with a pressure contact. Both types of contact remained stable when heated to 470°C for three days. However, both increased in resistance when heated to 520°C for one week. The resistance of the pressure contact increased at a faster rate than that of the bonded contact. It is concluded that these contacts will eventually deteriorate under prolonged operation above 500°C but that they will exhibit high stability when operated at about 450°C.

II-B. SILICON-GERMANIUM ALLOYS

A power generating thermocouple was made using Ge-Si alloys as the n- and p-type thermoelements. The cold junctions were maintained at 31°C by water cooling. The hot junction temperature was maintained by an electrical heater in the form of a rectangular molybdenum box. The heating elements consisted of thin ceramic plates metallized in a

resistive pattern. The dimensions of the heater were $3/8 \times 3/8 \times 1/4$ inch, and the thermoelements were $1/4 \times 1/4 \times 1/2$ inch. The hot junction contacts consisted of a thin layer of indium which became liquid at high temperatures. Radiation and conduction losses were reduced by surrounding the couple with fine zirconia powder and operating the generator in vacuum. The temperatures were measured by means of Pt-Pt 13% Rh thermocouples welded to the heater and the cold junction metal, and the thermoelectric voltage was measured with respect to Pt.

The performance of the couple under maximum efficiency conditions was measured with the hot-junction temperatures at 640, 780, and 870°C. The conversion efficiency, η , (power out/heat in), current, I , and delivered power, P , together with the couple resistance, R , and heat-flow, $K\Delta T$, are shown in Table II-1. The calculated values were obtained from the properties of the individual materials using a treatment which has been recently developed⁽²⁾, while the experimental values are the results of direct measurements. The difference between the calculated and experimental values for η_m , I_m , and P_m are a consequence of the fact that the measured values of R were 50 - 60% higher than the calculated values. The discrepancy is attributed to contact resistance at the hot junction.

TABLE II-1
PERFORMANCE OF Ge-Si ALLOY THERMOCOUPLE
With $T_c = 31^\circ\text{C}$

PROPERTIES	$T_H = 640^\circ\text{C}$		$T_H = 780^\circ\text{C}$		$T_H = 870^\circ\text{C}$	
	Cal.	Exp.	Cal.	Exp.	Cal.	Exp.
η_m (%)	7.53	5.2	9.28	6.4	10.4	7.0
I_m (amp.)	12.1	8.0	14.0	9.1	15.2	10.4
P_m (watt)	1.74	1.05	2.62	1.66	3.27	2.16
R (ohm $\times 10^2$)	1.01	1.64	1.10	1.72	1.16	1.75
$K\Delta T$ (watt)	18.8	17.6	22.3	22.3	24.4	26.4

The experimental values of $K\Delta T$ increased with T_H more rapidly than the calculated values; at the lowest $T_H = 640^\circ\text{C}$ the experimental value of $K\Delta T$ was 6% lower than that calculated, while at $T_H = 870^\circ\text{C}$ the experimental value was 8% larger than the computed

value. This relative increase is attributed to radiation losses which naturally increase with increasing T_H . The fact that the experimental $K\Delta T$ falls below the calculated value at $T_H = 640^\circ\text{C}$ may be due to some random errors in the measurement of κ for the materials (used in the calculations) and in the direct measurement of $K\Delta T$. Since both measurements were accurate to about 5%, a discrepancy of 7% between them is not unlikely. Thus the radiation loss is most likely no larger than 15% even at $T_H = 870^\circ\text{C}$.

The highest efficiency measured was 7.0% at $T_H = 870^\circ\text{C}$, while 10.4% was expected on the basis of the known properties of the materials. Most of the discrepancy is attributed to a large contact-resistance at the hot-junction. With the development by RCA, Electron Tube Division, of a process for bonding refractory metals to the Ge-Si alloys, much closer agreement with the calculated values of η_m is now possible.

Measurements were made on a single-stage thermoelectric generator in an apparatus designed for measuring efficiencies at various ambient temperatures. The extraneous resistance around the entire electrical circuit, due to leads, connections etc., totaled about 30% of the elements. The average of the measured conversion efficiencies between the operating temperatures of 330°C and 510°C was 1.33%. The analysis of the measurements indicated that 0.9 watts were consumed at the hot junction by Peltier heat, and 5.6 watts were transferred by conduction to the cold junction. The measured heat input was 8.6 watts, so that 2 watts represented heat losses. The thermoelectric voltage output at the operating temperature was 79 mv, near that predicted by the Seebeck coefficient. The percentage of heat lost is 23%, and the percentage of electrical energy dissipated in extraneous resistance is 22%. When these two principal energy losses are considered in the calculation, the conversion efficiency would then become 2.26% for the temperature range between 330°C and 510°C .

A method was developed for obtaining low resistance, ohmic contacts when bonding both n- and p-type Ge-Si alloys to a metallic electrode. The n-type face to be bonded was first electroless nickel plated, then heated in dry hydrogen at 800°C for 10 minutes. The face was again plated, and then bonded to the metallic electrode with a silver solder. Room temperature contact resistance on three such bonds were all less than 2% of the resistance of the n-type alloy elements. The p-type contact was made with an aluminum bond to the metallic electrode. The total room temperature resistance of the four contacts was less than 6% that of the elements.

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